2017 DOE AMR

Research and Advanced Engineering

Next Generation Three-Way Catalysts for Future, Highly Efficient Gasoline Engines

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Ford Research and Advanced Engineering

8-Jun-2017

Project ID: PM067

Overview

Timeline

- Start Date: 1-Oct-2014
- End Date: 30-Sept-2017
- Status: ~ 90% complete

Budget

- Total funding: $1,690,470
  - DOE share: $752,376
  - Contractor share: $338,094
  - Additional ORNL $600,000
- Funding in FY 2016 (actual)
  - $273,150
- Funding in FY2017 (est.)
  - $ 193,646

Barriers

- Long lead times for materials commercialization
- Cost

Partners

- Ford Motor Company
- Oak Ridge National Lab
- University of Michigan
- Johnson Matthey, Inc. (non-funded)

Relevance

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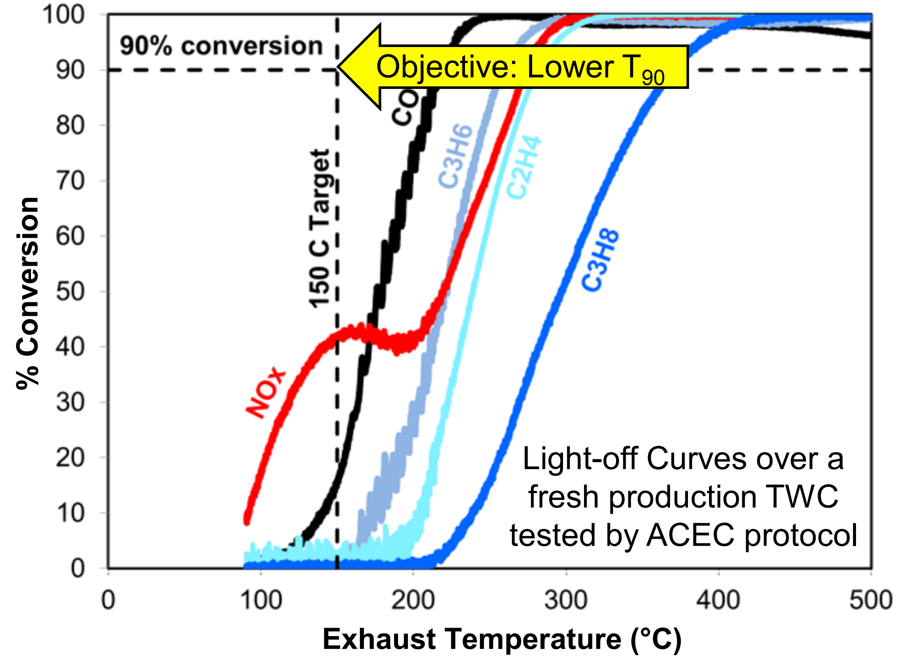
Overall Objective

- Develop new three-way catalysts and/or catalyst systems capable of achieving durable 90% activity [HC, CO, NOx] at 150°C.
  - Today's automotive three-way catalysts (TWCs) become highly efficient only when exhaust temperatures reach 250-400°C.
  - The next generation of engines will be more efficient and thus produce cooler exhaust at low load conditions
  - *TWC activity will be required at lower temperatures to satisfy strict emission standards*



Current Budget Year Objectives

- Scale-up to monolith cores for shorter lead time
- Complete tech transfer and file program IP for shorter lead time
- Predict vehicle performance and cost relative to commercial benchmark

FY17 Milestones

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Milestone	Status
Confirm materials and synthesis details with coater • Kickoff meeting was held between Ford, ORNL, UM, and JMI on August 25, 2016. Monthly meetings followed in 4Q16. Quantities of catalyst material necessary to washcoat monolith cores were discussed. Discussion on synthesis details and possible modifications occurred.	Completed Dec 2016
New monoliths vs. commercial TWC • Monolith washcoat process was started. JMI completed a powder reactor round robin with a commercial TWC to confirm partner systems operate similarly.	Ongoing
Technology transfer and secure program-related IP • ORNL disclosure 201603729, DOE S-138,375, Jae-Soon Choi, James E. Parks, II, Eleni Kyriakidou, Michael J. Lance and Todd J. Toops, “Emissions control catalysts with improved durability and low-temperature activity using enhanced metal-oxide supports.” • US patent application 15427618, CATALYST FOR AUTOMOTIVE EMISSIONS CONTROL, Andrew Getsoian, Joseph Theis, Christine Lambert, 8 Feb 2017.	Ongoing
System Model Assessments • Detailed reaction regime data will be used to predict tailpipe emissions using one or two leading formulations.	Due Sept 2017
Cost Model Assessments • Directional finished catalyst costs will be estimated for one or two leading formulations.	Due Sept 2017

Approach

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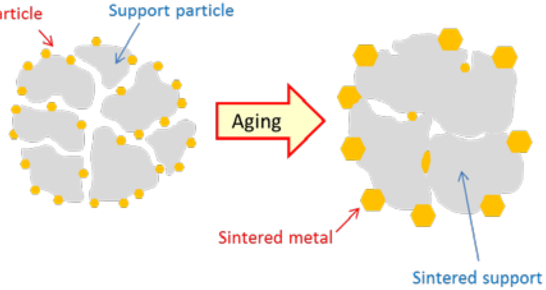
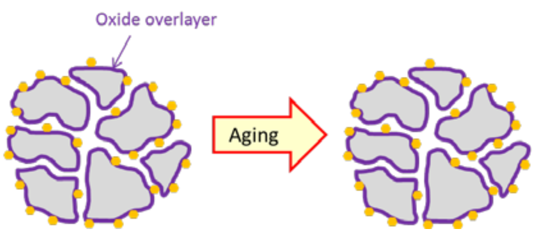
- Identify strategies to improve precious metal dispersion and promote activity
- Make and characterize new materials, and predict performance and **costs**
- Partner with major catalyst supplier for scale-up with **shorter lead time**

Oxide overlayer on oxide support

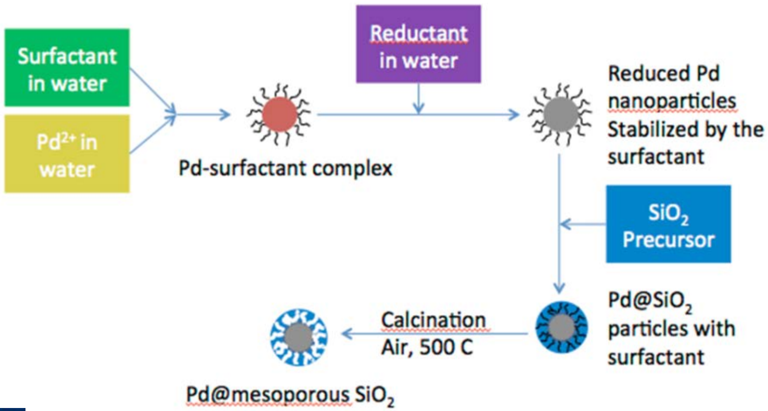
Challenge:
Prolonged exposure to high temperature automotive exhaust gases leads to sintering of both active metal and support, leading to loss of activity



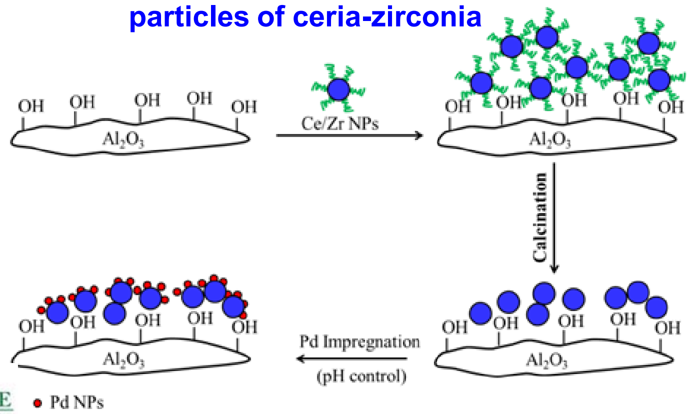
Approach:
Overcoat a high surface area oxide with a second oxide layer to reduce sintering and promote precious metal activity



One-pot synthesis of Pd@SiO$_2$ core-shell catalyst

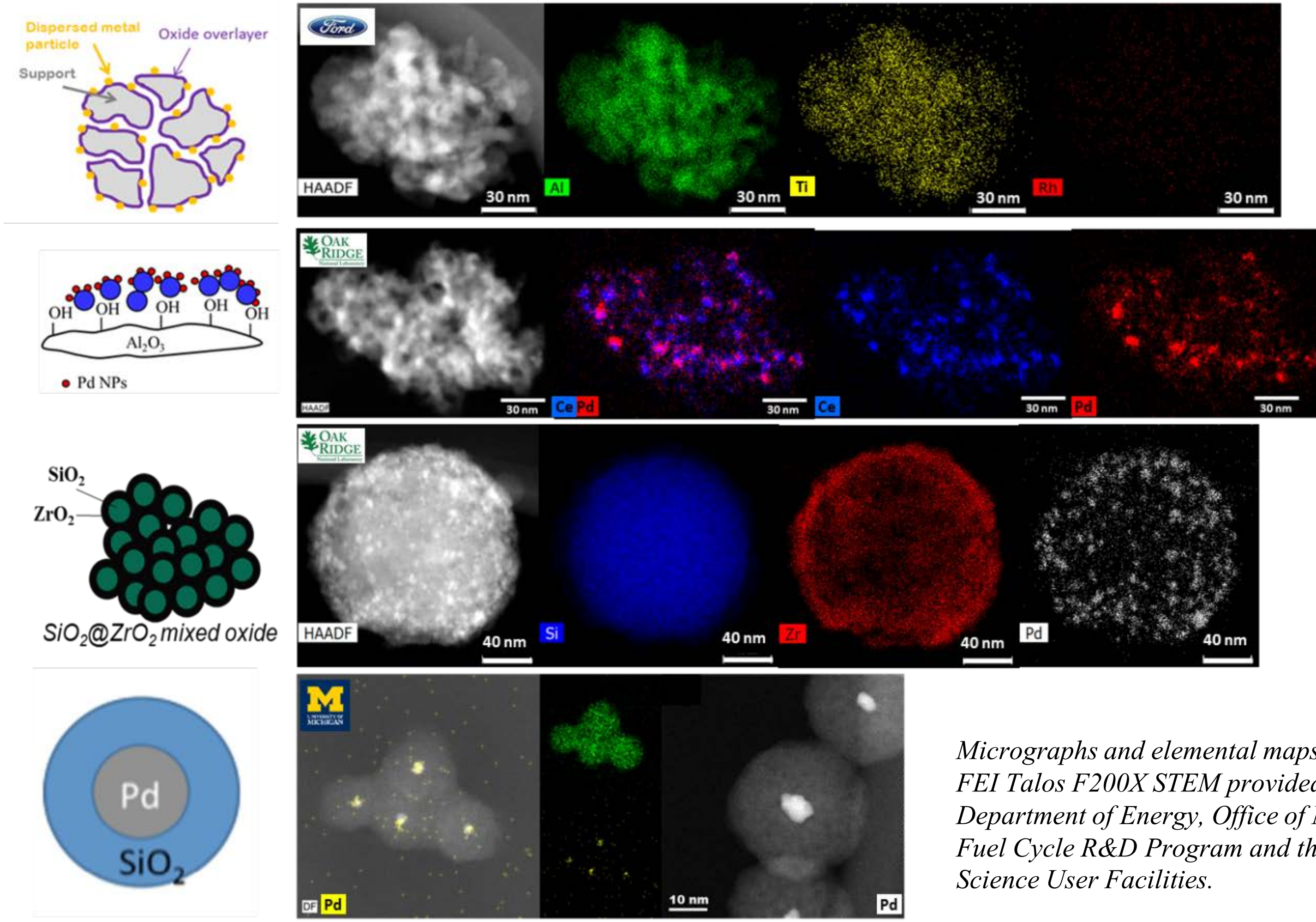


Improved dispersion and enhanced low temperature activity on using nanophase particles of ceria-zirconia



Accomplishments

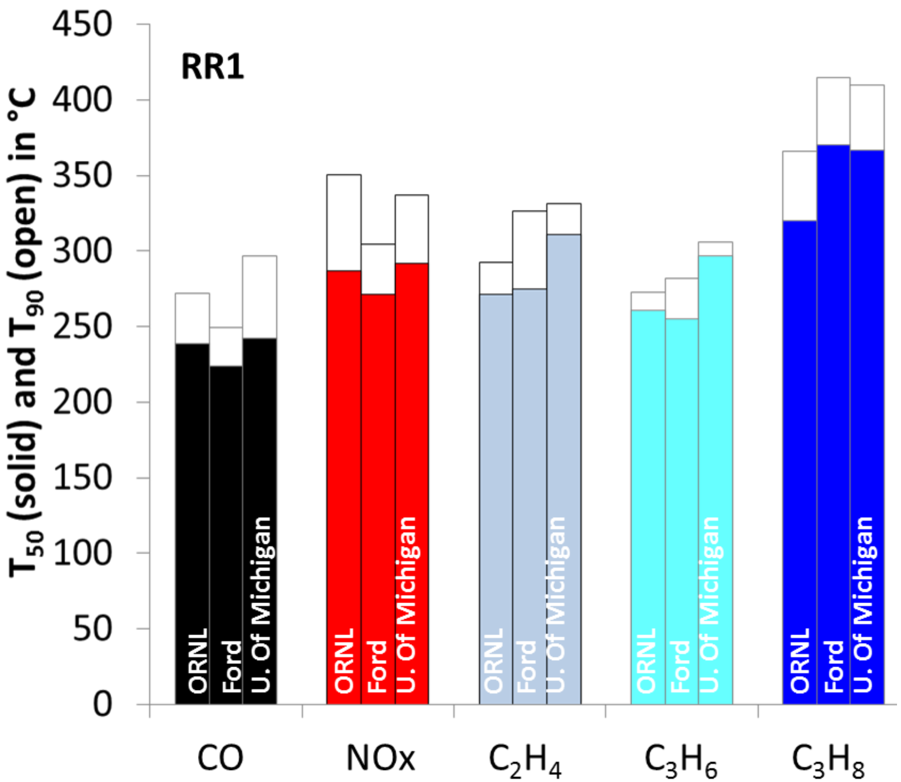
Research and Advanced Engineering

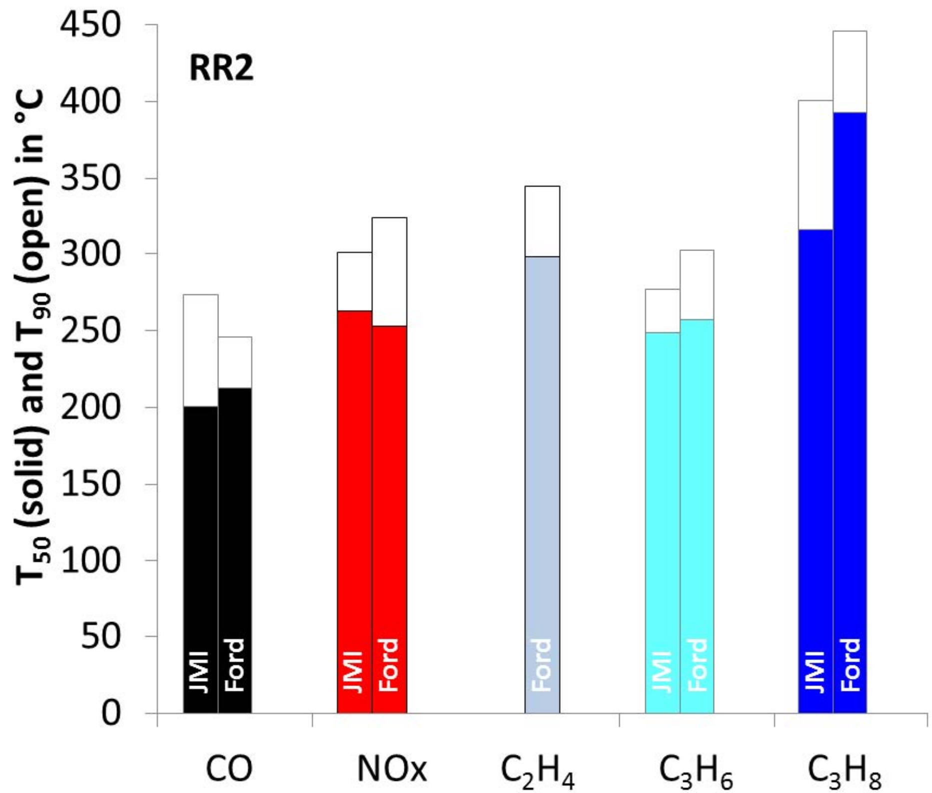


Micrographs and elemental maps recorded with FEI Talos F200X STEM provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities.

Confirmation of catalyst structures using the Talos electron microscope at ORNL

"Round Robins" confirmed reactor similarities with aged modern TWCs.



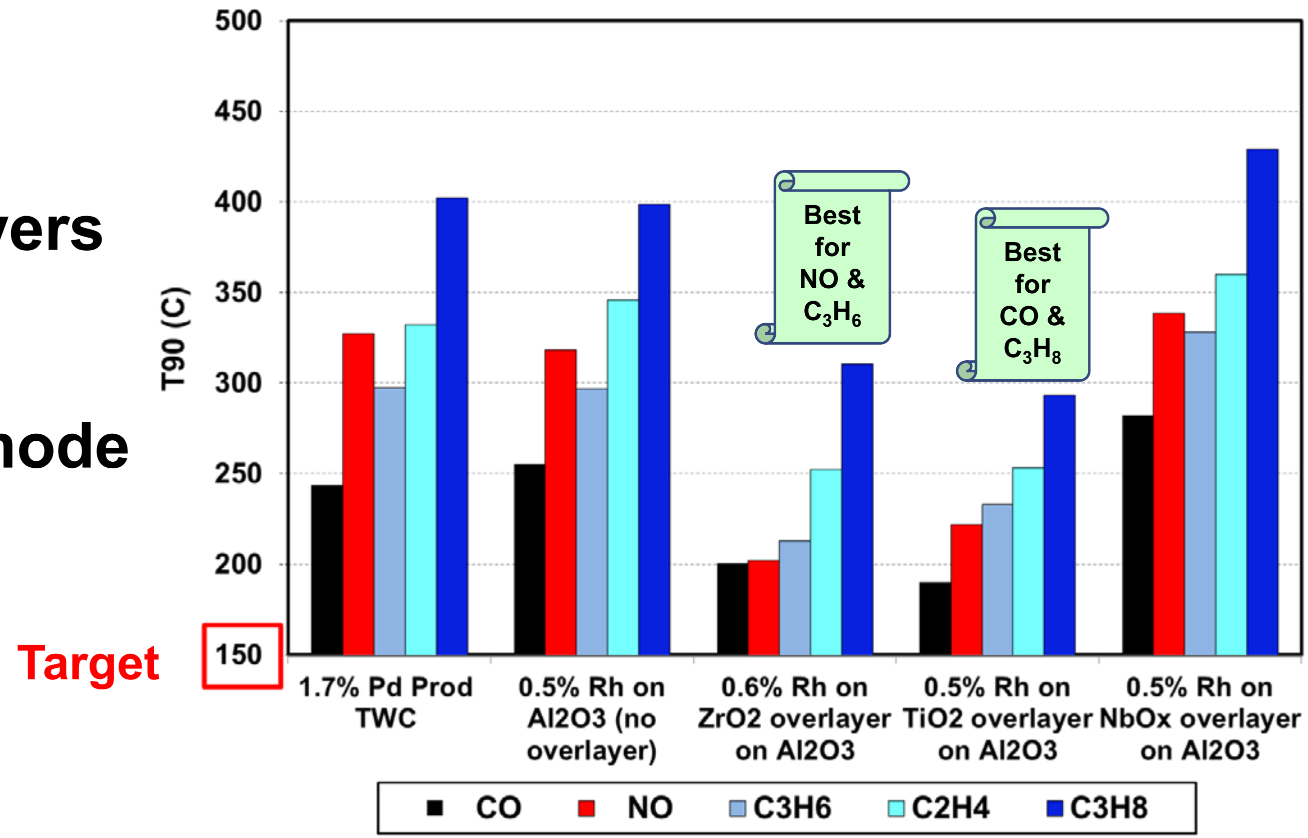


ACEC stoich protocol:

$[H_2O]$ = 10%	$[O_2]$ = {stoichiometric}	$[CO_2]$ = 10%	[NO] = 1000ppm
[CO] = 5000ppm	$[C_3H_8]$ = 150ppm	$[C_3H_6]$ = 500ppm	$[C_2H_4]$ = 525ppm
$[H_2]$ = 1700ppm	N_2 or Ar Balance	0.2 – 3.4 slm flow	0.1 – 2.0 g crushed monolith

Accomplishments

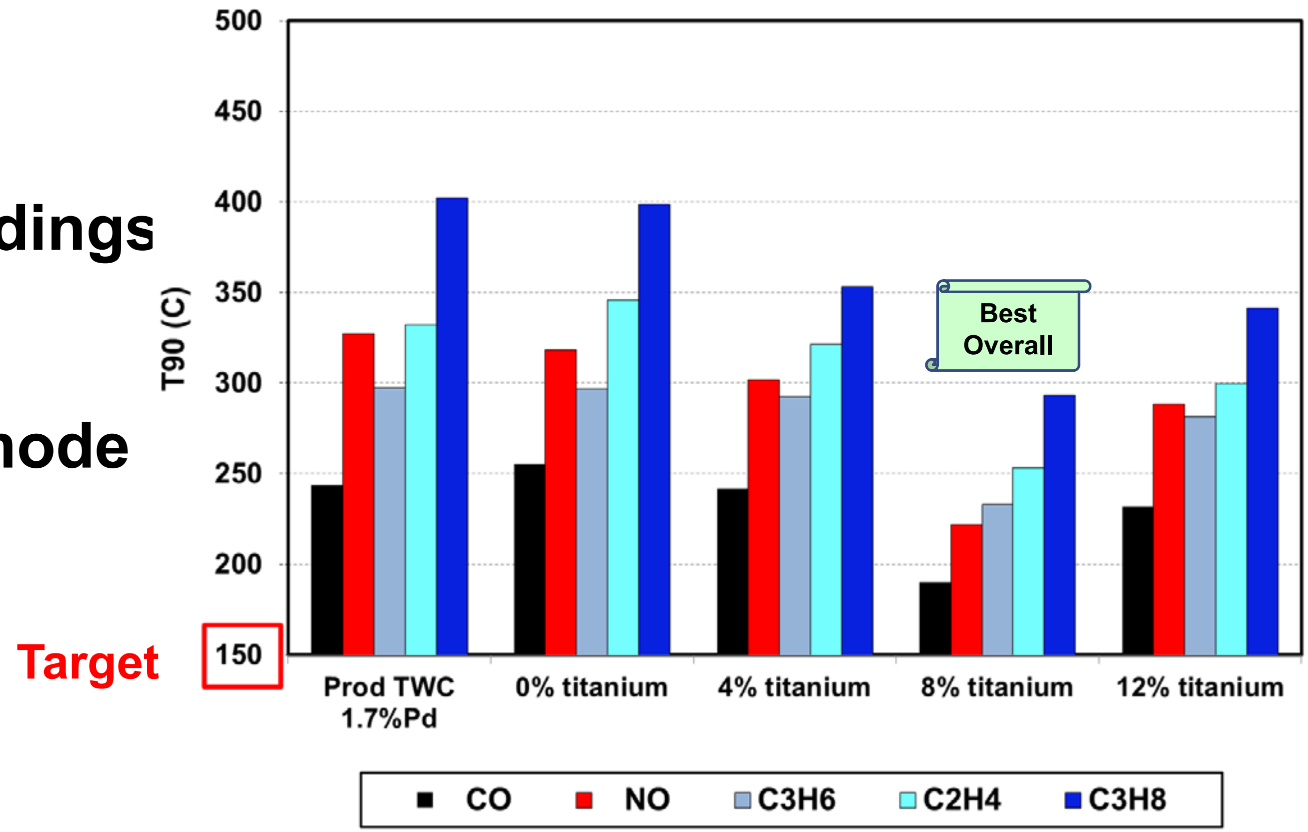
- 0.5-0.6% Rh
- Varied overlayers
- Al_2O_3 support
- Aged: 50h 4-mode
- 960°C max



The titania and zirconia overlayers had significantly lower T90s than production TWC and non-overlayer catalyst

Accomplishments

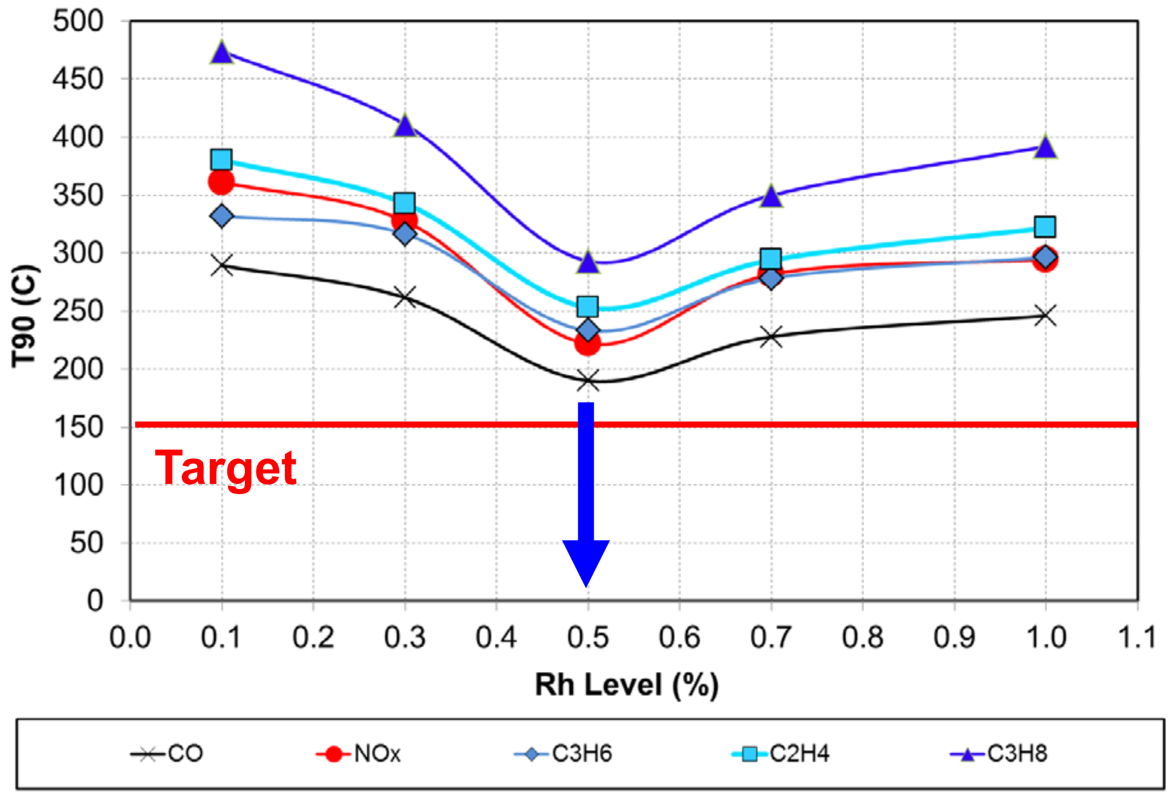
- 0.5% Rh
- Various Ti loadings
- Al_2O_3 support
- Aged: 50h 4-mode
- 960°C max



The 8% titanium loading had the lowest T90s after aging; corresponds to the monolayer coverage of TiO_2

Accomplishments

- **Varied Rh**
- **8% Ti**
- **Al_2O_3 support**
- **Aged: 50h 4-mode**
- **960°C max**



- **The lowest T90s achieved with 0.5% Rh at 8% Ti**
- **Downselected as our prime formulation for scale-up**

Accomplishments

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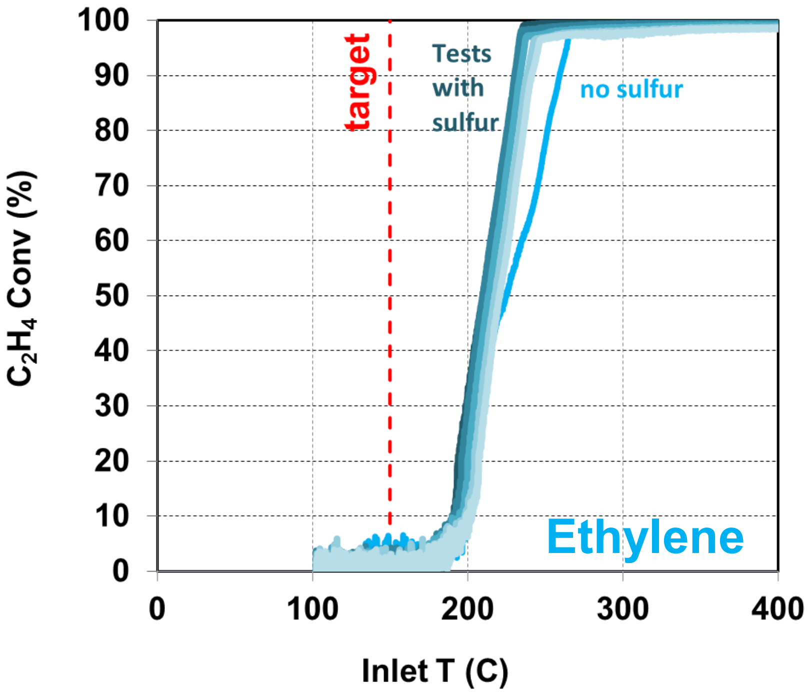
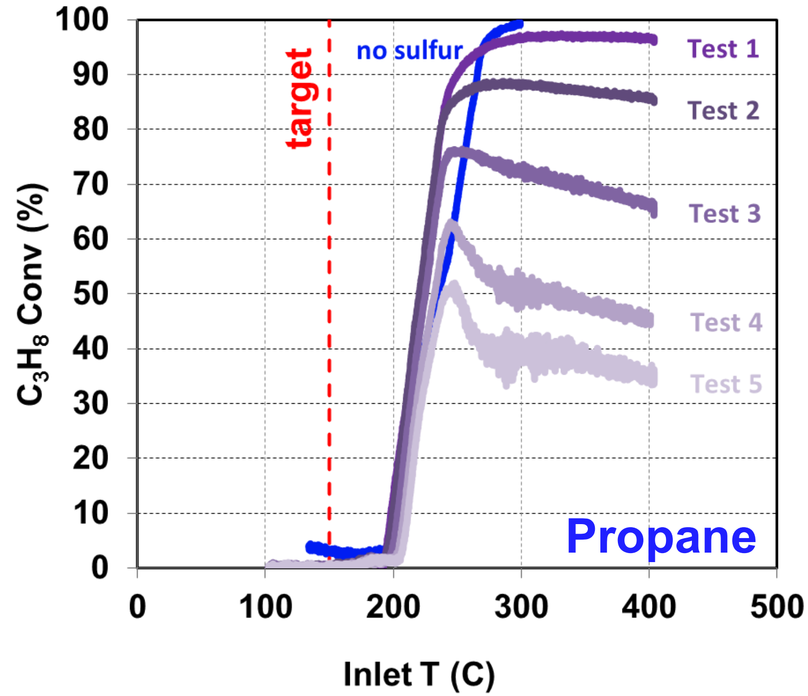
SO_2 Poison Study, 5 Ramps 100 to 400 to 100°C, 5 ppm SO_2 Degreened 0.5% Rh on 8% Titanium on Al_2O_3

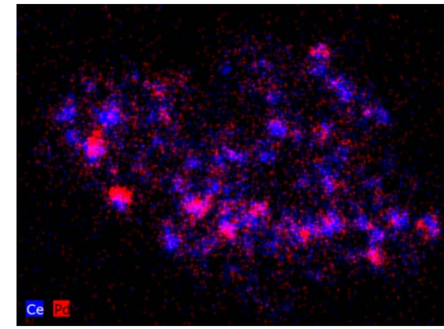


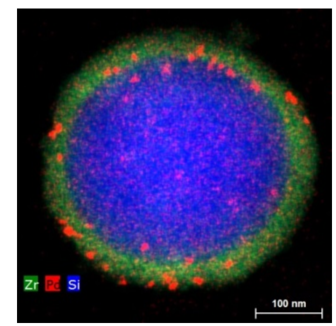


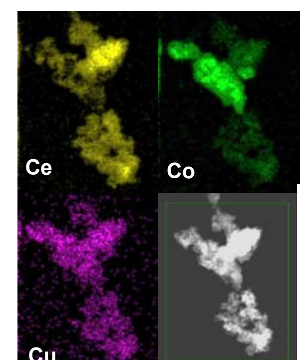
- Large effect on propane conversion; can be recovered (deSOx)
- Periodic exposure to 600°C mitigated SO_2 effects on propane
- Similar trends for 4-mode aged sample
- Zr version did not deSOx as easily as Ti version; downselect alternative

ORNL pursued three pathways

- **Targeted deposition of PGM on islands of metal oxide nanoparticles on high surface area support**
  - Ceria and ceria-zirconia nanoparticles initially studied
  - Most promising technology developed at ORNL
    - **Pd/nanoCe-Zr/Al_2O_3 is the downselected technology**
    - **Aged 900°C under stoichiometric conditions**
- **Metal oxide core@shell as PGM support**
  - Maximize coverage of optimal metal oxide PGM-support on high surface area metal oxide, i.e. silica, alumina
  - PGM deposited on outside layer
  - Some promising results, but durability not better than commercial TWC → not chosen for downselect
- **Ternary metal oxide approach**
  - CO specialist, with minimal interaction with hydrocarbons
  - Showed potential NO adsorber capability under stoichiometric, but rate of uptake not fast enough
  - Not thermally stable enough; not chosen for downselect





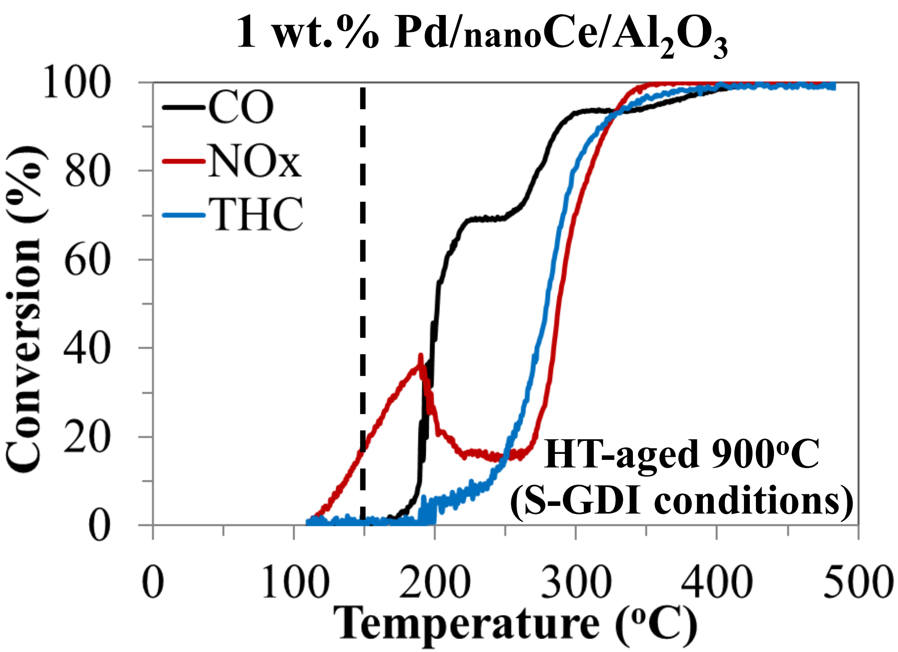


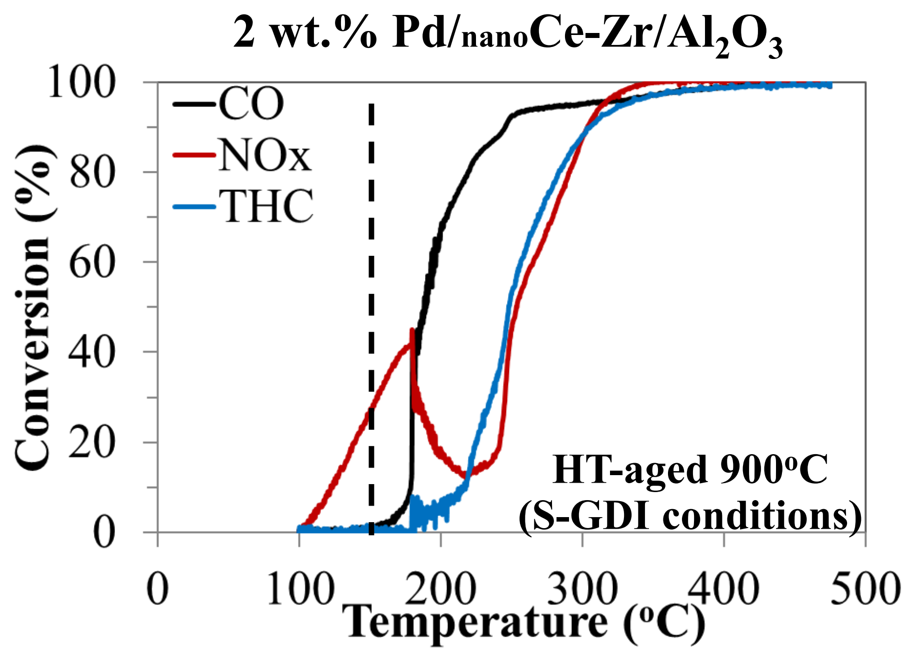
Accomplishments

Ford Research and Advanced Engineering

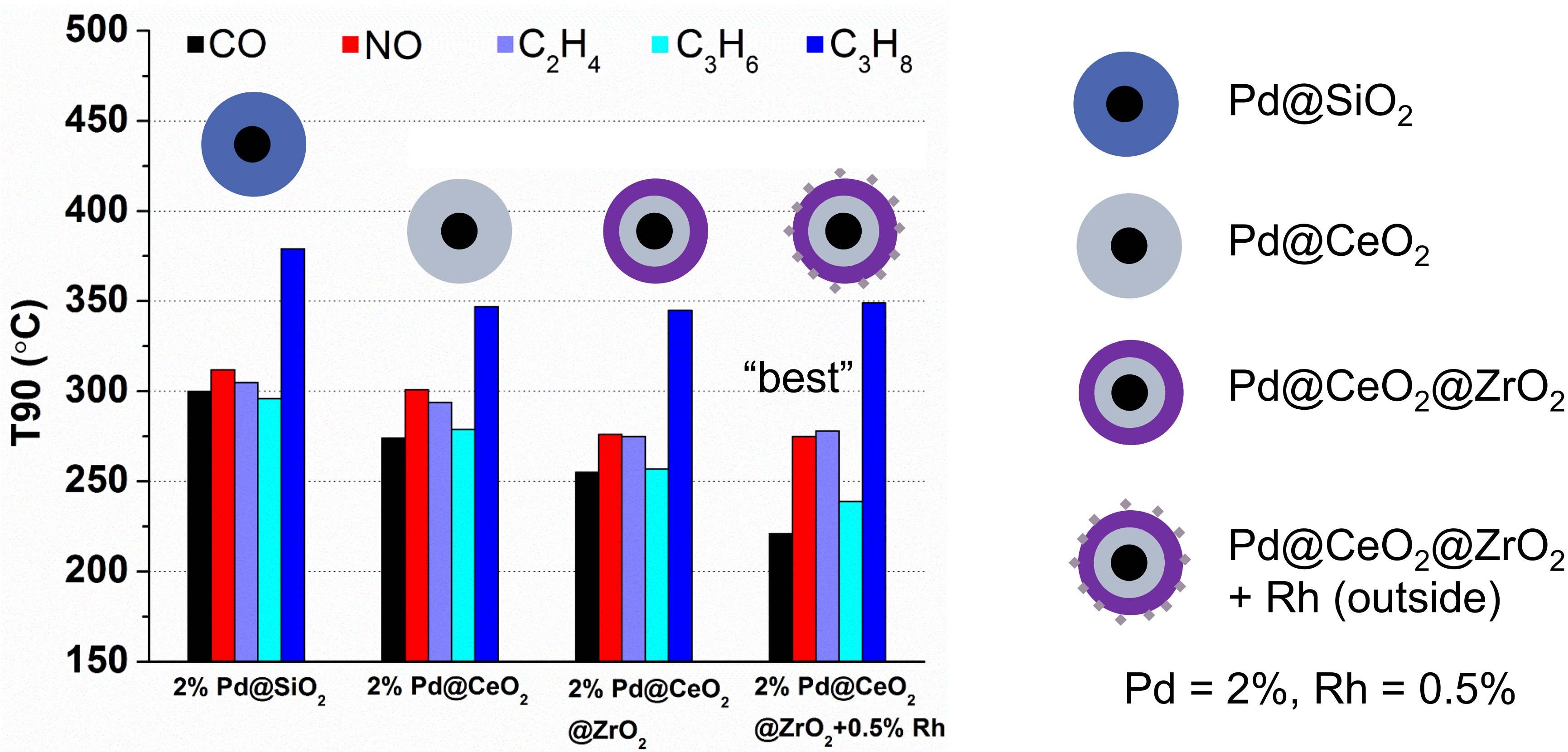
Promising results with targeted deposition of PGM on nano-CeO_2 and CeO_2-ZrO_2 samples

- Dispersing Pd on Ce has shown good low initial performance but thermal aging had significant effect
- Improved durability observed with Ce-Zr nanoparticle
  - 2% best of the 1-4% Pd samples evaluated





Performance comparison of Pd@CeO_2-based core@shell materials (Hydrothermally aged at 800°C)



Not tested with 960°C 4-mode aging; not downselected

Accomplishments

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DOWNSELECTED TECHNOLOGIES

	Commercial	PRIME	ALT 1	ALT 2
	1.7% Pd 960°C 4-mode aged	0.5% $Rh/TiO_2/Al_2O_3$ 960°C 4-mode aged	0.6% $Rh/ZrO_2/Al_2O_3$ 960°C 4-mode aged	2% Pd/ $_{nano}CeO_2$-ZrO_2/ Al_2O_3 900°C stoich aged
T90 (CO)	245°C	190°C (-55°C)	201°C (-44°C)	210°C (-35°C)
T90 (HC)	345°C	253°C (-92°C)	256°C (-89°C)	305°C (-40°C)
T90 (NO)	330°C	222°C (-108°C)	202°C (-128°C)	302°C (-28°C)

Although, none of these samples achieved 150°C aged T90s, results show meaningful progress towards this goal

Responses to Previous Year Reviewers' Comments

- **Parallel effort / multiple approaches / making materials / no black boxes**
  - Project includes materials previously used in auto catalysts but in new geometries
  - Enhance/stabilize higher precious metal surface area
  - Positive metal support interactions
  - Partners are making the materials themselves

- **Need better understanding of how poisons like sulfur affect the catalysts**
  - Sulfur was addressed directly in the recent work with $Rh/Ti/Al_2O_3$ and $Rh/Zr/Al_2O_3$
  - Most T90s were not impacted by sulfur exposure on a degreened catalyst
  - The only T90 directly affected was propane and was recoverable

- **Adequate resources/funding/staffing/cost share**
  - Funds are sufficient at this stage of research
  - More funds would potentially accelerate research and scale up of promising materials
  - Cost share at 20% seems fair given the risky nature of fundamental research
  - Project is appropriately staffed with catalyst experts at all collaborative partners
  - Project is on track and meeting milestones

Collaboration and Coordination with other Institutions

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Ford Motor Company

- Modified metal support materials with layered oxides
- Cost and performance models

Oak Ridge National Laboratory

- Modified support materials
- Ternary base metal oxides as PGM substitutes

University of Michigan

- Core@shell model catalysts

Johnson Matthey, Inc.

- Scale-up of most promising materials to washcoated cores
- Provide guidance on manufacturing feasibility and finished catalyst costs relative to a commercialized benchmark

Full collaboration between all partners including material transfer and cross lab characterization

Remaining Challenges and Barriers

- **Long lead times for materials commercialization**
  - Use materials with known, high stability in automotive exhaust
  - Use commercially available support materials as a base and add new materials onto base to support metals in novel ways
  - Partnership with major automotive catalyst supplier
- **Cost**
  - Develop stable, high surface areas for better metal dispersion
  - Focus more on Rh at low levels
  - Fewer processing steps
  - Aqueous solvents

Proposed Future Research

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- **Project is ending Sept 30, 2017**

- **The following work is planned:**
  - Scale-up of most promising materials to monolith cores
  - Compare monolith core performances to commercial benchmark
  - Complete technology transfer and secure program-related IP
  - Final system model assessment
  - Final cost assessment
  - Final project reporting

Any proposed future work is subject to change based on funding levels.

Summary

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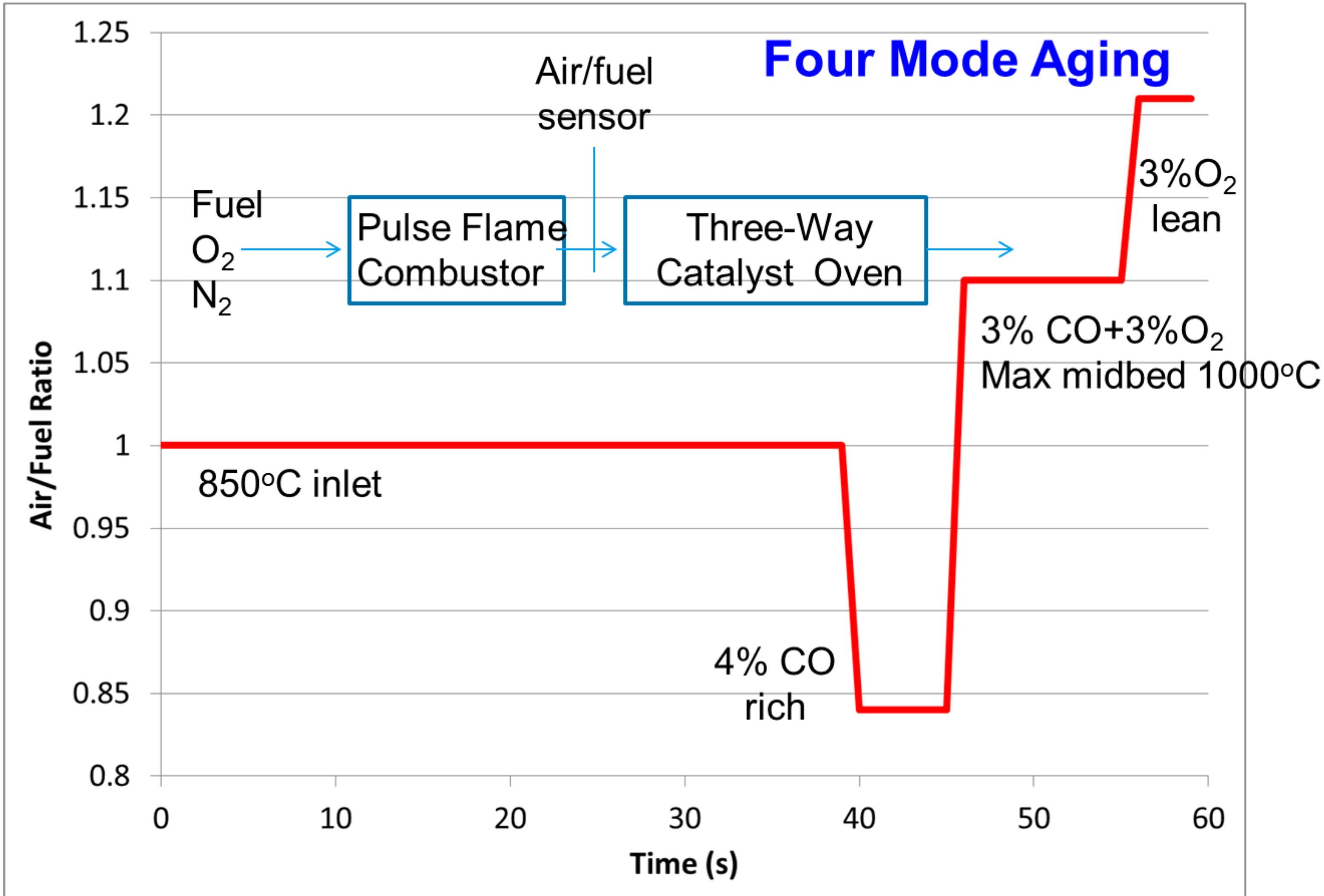
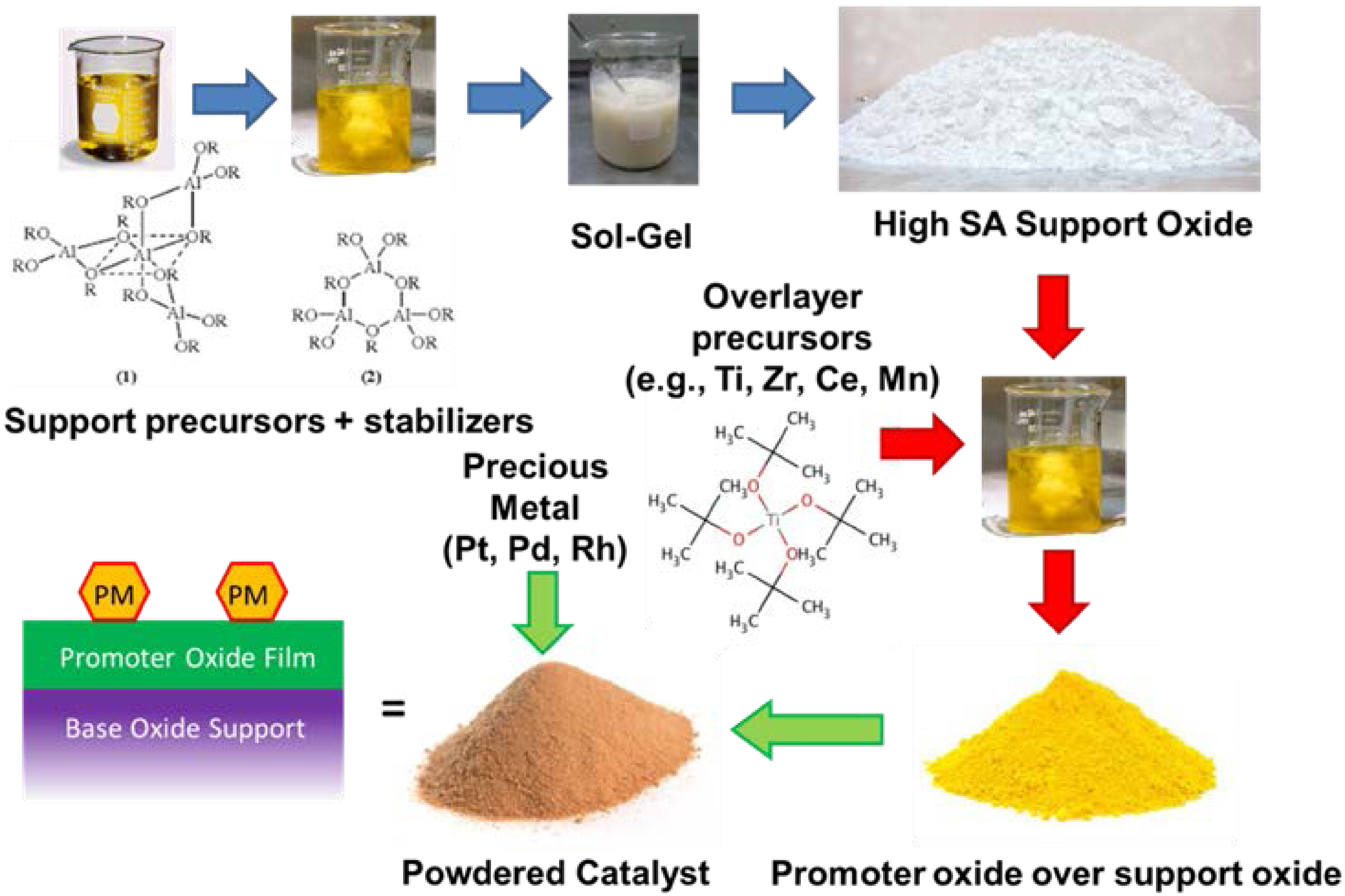
- **Approach:** Make and characterize new materials, and predict performance and costs; scale-up technology; assess manufacturability
- **Technical Accomplishments**
  - Commercial TWC “round robin” was used to demonstrate reactor-to-reactor compatibility amongst all four partners
  - Downselected materials (in ranking order):
    - 0.5 %Rh/8% Ti/Al_2O_3
    - 0.6% Rh/15%Zr/Al_2O_3
    - 2% Pd/nanoCe-Zr/Al_2O_3
  - Sulfur was addressed and affected propane conversion temporarily
- **Collaborations:** Full collaboration between Ford, UM, ORNL, JMI
- **Proposed Future Research:** Continue towards shorter lead times for materials commercialization and lower costs
- **Relevance:** TWC materials required to be active at lower temperatures to satisfy strict emission standards with the next generation of automobiles

Technical Backup


Four Mode Aging
Air/fuel sensor
Fuel
O_2
N_2
Pulse Flame Combustor
Three-Way Catalyst Oven
3%O_2 lean
3% CO+3%O_2
Max midbed 1000°C
850°C inlet
4% CO rich
Air/Fuel Ratio
Time (s)
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0
10
20
30
40
50
60

Synthesis of Layered Oxide Supported Catalysts

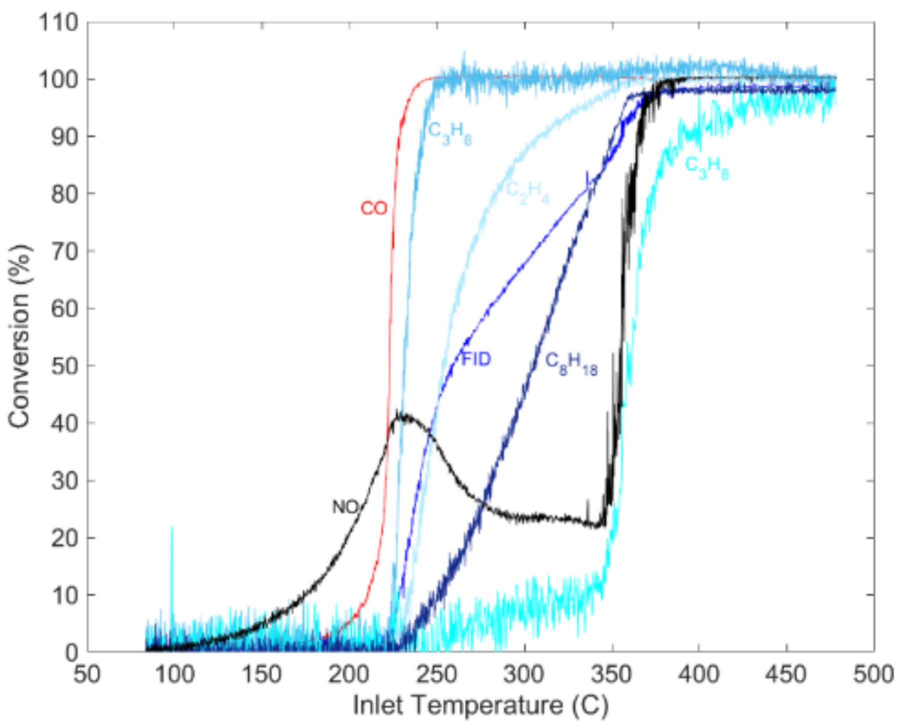


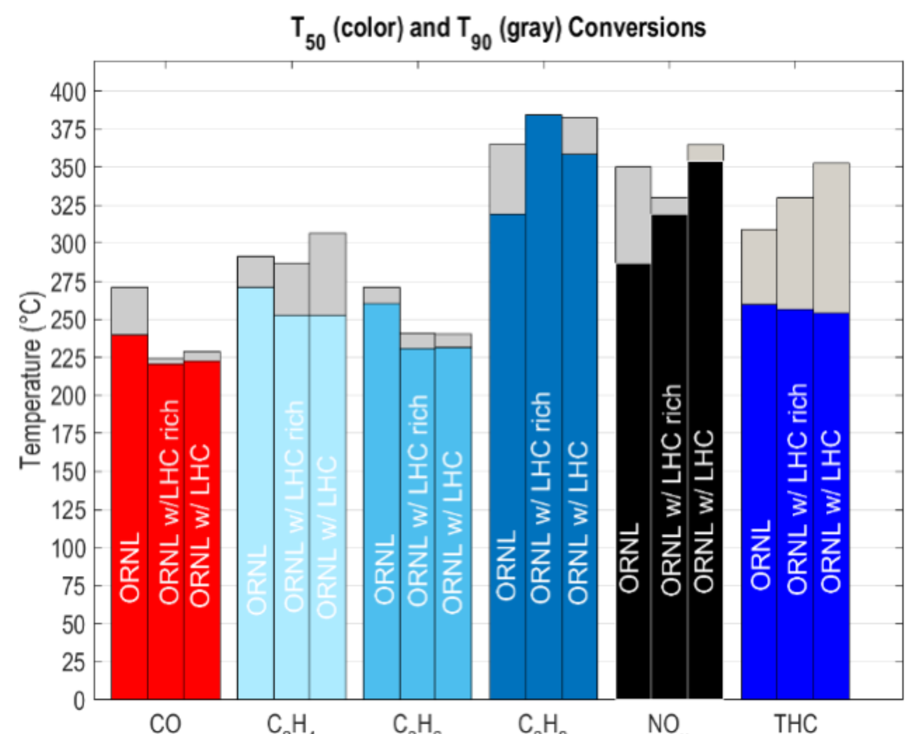
Liquid hydrocarbon comparison

- Employed ACEC protocol for liquid HC evaluation using iso-octane
- Repeated evaluation of TWC from round-robin and compared light-offs
- Generally good agreement with gas-only evaluation (ORNL in bar graphs)

Hydrocarbon Contribution to THC C_1

	w/ Iso-octane	Gaseous only
C_2H_4	700 / 23.3%	1050 / 35%
C_3H_6	1000 / 33.3%	1500 / 50%
C_3H_8	300 / 10%	450 / 15%
C_8H_{18}	1000 / 33.3%	---

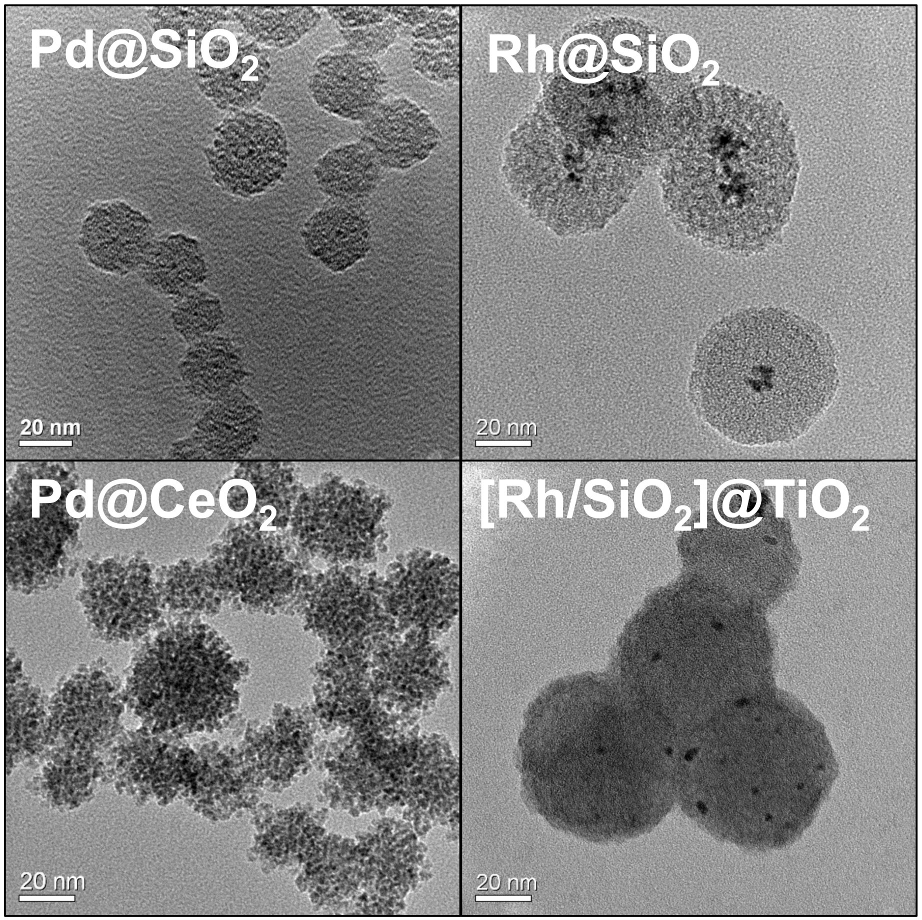




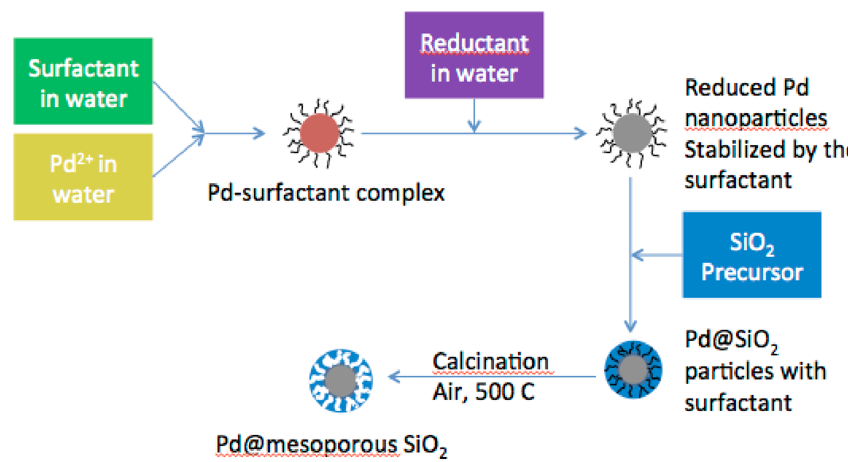
Technical Backup

Research and Advanced Engineering

Expanded number of one-pot core@shell materials prepared in past year



- Combinations of metal cores/oxide shells prepared via an aqueous one-pot method with tunable core and shell sizes
- Cores: Pd, **Rh**
- Shells: SiO_2, **CeO_2, TiO_2**
- Example of Preparation Approach: Pd@SiO_2



Improved thermal stability of CeO_2 shell

- CeO_2 normally forms larger particles at lower temperature (< 700 °C)

- Thermal stability of CeO_2 particles is improved by two strategies
  - Double-shelled structure ($Pd@CeO_2@SiO_2$, $Pd@CeO_2@ZrO_2$)
  - Solid-solution with ZrO_2 ($Pd@Ce_{.2}Zr_{.8}O_2$)

- Both strategies improve the CeO_2 thermal stability based on XRD
- Core@shell catalyst with CeO_2 shell exhibits much stronger peak sharpening only after aging to 700 °C